METHOD FOR CORROSION CONTROL OF REFINING UNITS
BY ACIDIC CRUDES

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The present invention relates to the field of the treatment of acid crude oils in refineries. A more particular subject-matter of the invention is a process for combating the corrosion of refining plants which treat acid crudes, 10 comprising the use of specific sulphur compounds.

Oil refineries may be confronted with a serious problem of corrosion when they are forced to treat certain "acid" crudes. These acid crudes essentially comprise naphthenic acids, which are the source of this very specific corrosion phenomenon since it occurs in a liquid medium which does 15 not conduct electrical current. These naphthenic acids correspond to saturated cyclic hydrocarbons carrying one or more carboxyl groups. The acidity of a crude oil is described by a standardized measurement according to Standard ASTM D 664-01. It is expressed in mg of potassium hydroxide necessary to neutralize 1 g of oil and is referred to as TAN (Total Acid Number). It is known 20 in this technical field that a crude oil having a TAN of greater than 0.2 is described as acidic and can result in damage in the plants of a refinery.

This corrosion reaction is highly dependent on the local conditions, such as, for example, the temperature and the metallic nature of the wall in the plant concerned, the space velocity of the hydrocarbon and the presence of a 25 gas-liquid interface. Thus, even after many studies on the subject, refiners encounter great difficulties in predicting the scale of the corrosion reactions and their location.

One of the industrial solutions to this corrosion problem consists in using installations made of stainless steels or alloys of iron with in particular 30 chromium and molybdenum. However, this solution is not used to any great extent because of the high capital cost. Furthermore, this choice preferably has to be contemplated during the design of the refinery as stainless steels exhibit inferior mechanical properties to those of the carbon steels which are normally

used and require an appropriate infrastructure.

The consequence of the existence of these technical difficulties in treating acid crudes is thus that these crudes are generally sold to refiners at a lower price level than that of standard crudes.

5   Another solution to the problem of the treatment of an acid crude oil, used by refiners in practice, consists in diluting it with another non-acid crude oil, so as to obtain a low mean acidity, for example less than the threshold for TAN of 0.2. In this case, the concentration of naphthenic acid becomes sufficiently low to generate acceptable rates of corrosion. However, this

10   solution remains limited in scope. This is because some acid crudes exhibit TAN values of greater than 2, which puts an upper limit on their use of at most 10% of the total volume of crudes entering the refinery. Moreover, some mixtures of crudes sometimes result in the reverse effect desired, even after dilution, that is to say in an acceleration in the corrosion reactions by

15   naphthenic acids.

Another approach in combating this corrosion problem is the introduction into the acid crude oil to be treated of chemical additives which inhibit or prevent attack on the metal wall of the plant concerned. This route is often very economical in comparison with that consisting in using the special

20   alloys or steels indicated above.

Laboratory studies, such as that of Turnbull (Corrosion - November 1998 in Corrosion, Volume 54, No. 11, page 922), have envisaged the addition of small amounts (of the order of 0.1%) of hydrogen sulphide to the crude oil in order to reduce corrosion by naphthenic acids. However, this solution is not

25   applicable in a refinery as hydrogen sulphide, which is a gas at ambient temperature, is highly toxic, which renders the consequences of an escape extremely serious and restricts the use thereof. Furthermore, at a higher temperature, hydrogen sulphide itself becomes highly corrosive and will result, in other parts of the refinery, in a worsening of generalized corrosion.

30   Patent US 5 182 013 discloses the use of other sulphur compounds in solving this same corrosion problem, namely polysulphides with alkyl radicals comprising 6 to 30 carbon atoms.
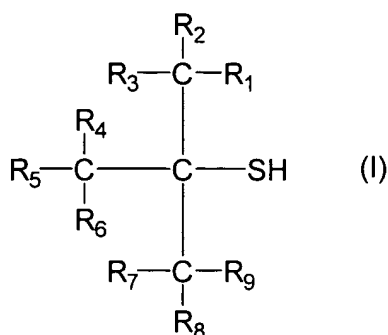
More recently, the use of corrosion inhibitors based on sulphur and on phosphorus has also been disclosed.

Thus, Patent EP 742 277 discloses the inhibiting action of a combination of a trialkyl phosphate and of an organic polysulphide. Patent US 5 552 085 recommends the use of thiophosphorus compounds, such as organothiophosphates or organothiophosphites. Patent AU 693 975 discloses, as inhibitor, a mixture of trialkyl phosphate and of phosphoric esters of sulphurized phenol neutralized with lime.

However, organophosphorus compounds are very problematic to handle due to their high toxicity. Furthermore, they poison the hydrotreating catalysts installed to purify the hydrocarbon fractions resulting from atmospheric and vacuum distillations. For these two reasons, at least, their use in the field of refining is not desirable.

Crude oils comprise a great variety of organosulphur compounds, including alkyl mercaptans. Surprisingly, it has been found that a specific family of alkyl mercaptans, the compounds in which the mercaptan functional group is carried by a tertiary carbon, make it possible to inhibit corrosion by naphthenic acids more effectively than organic polysulphides and without it being necessary in addition to introduce phosphorus-comprising inhibitors.

A subject-matter of the invention is thus a process for combating the corrosion by naphthenic acids of the metal walls of a refining plant in which a hydrocarbon stream is treated in the absence of oxygen, characterized in that it comprises the addition to the said stream of an effective amount of one or more hydrocarbon compound(s) comprising from 4 to 20 carbon atoms of formula:

$$
\begin{array}{c}
R_2 \\
| \\
R_3-C-R_1 \\
R_4 \quad\quad | \\
| \quad\quad\quad | \\
R_5-C\text{------}C\text{------}SH \quad\quad (I) \\
| \quad\quad\quad | \\
R_6 \quad\quad | \\
R_7-C-R_9 \\
| \\
R_8
\end{array}
$$

in which the symbols R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8 and R_9, which are

identical or different, each represent a hydrogen atom or a linear or branched alkyl radical, an aryl radical or an alkylaryl radical, it being possible for these radicals optionally to comprise one or more heteroatoms, such as oxygen or sulphur.

5   The mercaptans preferably used according to the invention are tertiary mercaptans of empirical formula C_nH_{2n+1}-SH in which n is between 8 and 14.

      tert-Dodecyl mercaptan is a more particularly preferred compound of formula (I), taken in isolation or in the form of a complex mixture comprising tertiary mercaptans of 10 to 14 carbon atoms in which it is present at a content
10 of greater than 50% by weight. Such a mixture is generally prepared industrially by addition of hydrogen sulphide to an olefin fraction, such as tetrapropylene, and is sold under the name tert-dodecyl mercaptan.

      The amount of compound(s) of formula (I) to be added to the hydrocarbon stream to be treated by the refining plant generally corresponds to
15 a concentration, expressed as equivalent weight of sulphur in the said compound with respect to the weight of the hydrocarbon stream, of between 1 and 1000 ppm, preferably between 5 and 200 ppm. It will be possible, while remaining within this concentration range, to set a high content at the start of the process according to the invention and then subsequently to reduce this
20 content to a maintenance dose.

      The process according to the invention advantageously makes it possible to treat hydrocarbon streams, in particular crude oils, having a TAN of greater than 0.2 and preferably of greater than 2.

      The temperature for implementing the process corresponds to that at
25 which the corrosion reactions by naphthenic acids occur and is generally between 200 and 450°C and more particularly between 250 and 350°C.

      The addition of the compound of formula (I) to the hydrocarbon stream can be carried out either at the actual inlet of the plant (simultaneously with the hydrocarbon stream to be treated), for an overall treatment of the corrosion, or
30 in the part of the plant where the corrosion reaction takes place, for localized treatment. This addition can be carried out by any means known to a person skilled in the art which provides control of the injection flow rate and good dispersion of the additive in the hydrocarbon, for example using a nozzle or a mixer.

35   The term "metal walls of the refining plant", the corrosion of which can be prevented by the process according to the invention, is understood to mean

all the walls liable to be in contact with the acid hydrocarbon stream to be treated. The wall can thus be equally well the inner wall proper of plants, such as atmospheric and vacuum distillation towers, and the surface of the components internal to the latter, such as their plates or packings, or else of the components peripheral to the latter, such as their withdrawal and inlet lines or the pumps, preheat furnaces or heat exchangers, provided that these components are brought to a local temperature of between 200 and 450°C.

The metal employed in the manufacture of the walls of the refining plant is generally a carbon steel optionally comprising up to 10% by weight of chromium and/or of molybdenum, preferably up to 5%.

Nonlimiting examples of the hydrocarbon stream to be treated in accordance with the process according to the invention are crude oil, atmospheric distillation residue, the gas oil fractions resulting from atmospheric and vacuum distillations, and the vacuum residue and distillate resulting from vacuum distillation.

The following examples are given purely by way of illustration of the invention and should not be interpreted with the aim of limiting its scope.

In these examples, use is made of a corrosion test, the conditions of which are given below.

Description of the corrosion test:

This test employs an iron powder, which simulates a metal surface, and a mineral oil in which a mixture of naphthenic acids is dissolved, which simulates an acid crude stream. The characteristics of these reactants are as follows:

- white mineral oil having a density of 0.838,

- powder formed of spherical iron particles having a particle size of -40+70 mesh (i.e. of approximately 212 to 425 µm),

- mixture of naphthenic acids having from 10 to 18 carbon atoms, a boiling point of between 270 and 324°C and an average molar mass of 244 g/mol.

The following are introduced into a 150 ml glass reactor equipped with a dropping funnel and a water-cooled reflux condenser and provided with a

stirring system and a system for measuring the temperature:

- 70 ml (i.e. 58.8 g) of the mineral oil,

- 2 g of the iron powder,

- 2.8 g of the naphthenic acid mixture.

5   The initial TAN of the reaction mixture is 10.

These reactants are kept in contact for 2 hours at a temperature of 250°C under a dry nitrogen atmosphere to prevent oxidation reactions.

At the end of the test, the concentration of dissolved iron in the medium is determined by a conventional method in which a sample is digested, the

10   residue is taken up in acidified water and assaying is carried out using a plasma torch.

This concentration of dissolved iron (expressed in ppm) is directly proportional to the rate of the corrosion of the iron powder generated by the mixture of naphthenic acids present in the mineral oil.

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Example 1 (Comparative): Reference test in the absence of inhibitor

The preceding test is carried out without addition of compound of

20   formula (I), with 2 repetitions.

The results are shown in Table I below.

<u>Table I</u>

	Iron concentration (ppm)
Test 1	180
Test 2	227
Mean	203.5

25   **EXAMPLE 2: Tests in the presence of tertiary alkyl mercaptans**

Example 1 is repeated while adding to the mineral oil, during the charging of the reactor, tert-nonyl mercaptan or tert-dodecyl mercaptan. These products are mixtures of tertiary alkyl mercaptans centred respectively on the compounds comprising 9 and 12 carbons. The content of these derivatives is calculated so as to obtain a corresponding concentration of 500 ppm by weight of sulphur in the mineral oil present in the reactor.

The results collated in the following Table II are obtained.

The degree of inhibition of the corrosion brought about by the naphthenic acid mixture has also been shown in this table. This degree is expressed in % and is defined by the formula:

$$inhibition \ (\%) = \left(1 - \frac{[Iron] \ with \ inhibitor}{[Iron] \ without \ inhibitor}\right) \times 100$$

in which [Iron] is the concentration of dissolved iron, measured with or without inhibitor, the concentration of iron without inhibitor being 203.5 ppm in accordance with Example 1.

Table II

Compound of formula (I)	Iron concentration (ppm)	Degree of inhibition (%)
tert-Nonyl mercaptan	48	76%
tert-Dodecyl mercaptan	<0.2	> 99.9%